polymer papers

Uranyl ions in perfluorinated (Nafion and Flemion) membranes: spectroscopic and photophysical properties and reactions with potassium hydroxide

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Absorption spectra, luminescence spectra and excited-state lifetimes of uranyl ions (UO_2^{2+}) incorporated in Nafion or Flemion membranes have been studied as a function of hydration. Marked changes in the nature of the spectra and emission lifetime are observed. Thus at 291 K the lifetime changes from 2.0 μs in a water-swollen Nafion membrane to 640 μs in a thoroughly dried sample. The lifetime of the dried sample is temperature-invariant, whereas those of heavily hydrated samples show activation energies of $30 \pm 2\,kJ\,mol^{-1}$, suggesting that water plays a key role in the excited-state deactivation. A changeover in the decay mechanism is found for samples of intermediate water content. Energy transfer from excited UO_2^{2+} to Eu^{3+} is observed, the effect being enhanced by membrane dehydration and being much more pronounced for Flemion membranes than for Nafion. Treatment of the UO_2^{2+}-containing membranes with aqueous KOH causes the formation of products concentrated near the membrane surface. The absorption spectra, luminescence spectra and X-ray diffraction of these materials have been compared with those of the oxides and uranates formed in solutions of various pH. Transmission electron microscopy reveals particles of less than 1 μm in size.

(Keywords: perfluorinated ionomers; Nafion; Flemion; emission lifetime; uranium; membrane-bound oxides)

INTRODUCTION

Perfluorosulphonate (such as Nafion) and perfluorocarboxylate (such as Flemion) membranes are finding an increasing number of applications in electrochemistry and catalysis[1,2]. The favourable properties of these materials are partly a consequence of their internal structure, and this has initiated a significant number of structural studies. The introduction of metal ions by ion exchange into these membranes allows the labelling of their hydrophilic zones and the probing of the local structure of the membrane, especially ion clustering. Thus changes in the morphology of Nafion and Flemion membranes by variation of parameters such as water content have been investigated by electron spin resonance (e.s.r.) and Mössbauer spectroscopy using membranes containing metal ions such as[3–6] Cu^{2+}, Fe^{2+} and Fe^{3+}. The use of UO_2^{2+} as a probe in such membranes should be of interest, given the known sensitivity of the absorption spectra and excited-state lifetime to changes in its environment such as hydration, coordination, pH, etc.[7–10]. As the species is a particularly heavy metal ion, it is also expected to be of interest as a label for the ionic domains of the membrane, possibly allowing their direct visualization by transmission electron microscopy.

Membranes containing microparticulate metal and metal oxide particles are beginning to be used as catalysts, as electrocatalysts and as solid polymer electrolytes[11–16]. One route to membrane-bound, finely divided, hydrated metal oxide particles is the reaction of metal-ion-containing membranes with hydroxide ion solutions, as has been demonstrated for Nafion containing Fe(III) and Ru(III/IV) ions[17–19]. The hydrated ruthenium oxide formed by this route has been shown to be an active electrocatalyst for reactions such as the reduction of oxygen to hydrogen peroxide and the oxidation of water to oxygen in modified electrodes[14]. The formation of microparticulate metal oxide particles by this method is expected to be dependent on a number of factors, such as the effective pH inside the membrane, the relative mobility of the alkali metal ion and the hydroxide ion, as well as the inherent chemistry of the metal in itself. As UO_2^{2+} is known to have a particularly rich chemistry in weakly acid and alkaline solution[7,20], a study of the membranes produced by treatment of UO_2^{2+}-containing Nafion membranes seemed of interest to learn more about the factors involved in the phenomenon of metal ion reactions with alkali in perfluorinated membranes.

EXPERIMENTAL

Materials

$UO_2(NO_3)_2 \cdot 6H_2O$ (Fluka or BDH Analar) and $Eu(NO_3)_3 \cdot 6H_2O$ (Tonzart & Matignon) were used as received. Nafion 117 (H^+ form), equivalent weight 1100, 0.19 mm thick (Dupont), was purified by treatment with 1:1 (v/v) ethanol:water for 1 h in an ultrasonic bath

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and subsequent thorough rinsing with deionized water. Flemion, molecular weight 599, was prepared by treating the ester form with 1 M KOH for 3 h at 90°C and subsequently with 1 M HCl for 16 h at 90°C.

Instrumentation

Electron microprobe analysis was carried out using a Camebax scanning electron microscope, with samples prepared as described earlier[14]. Transmission electron microscopy and electron microdiffraction were performed on ultra-thin sections (400–900 Å) using a Jeol EM100 CX II transmission electron microscope equipped with a goniometer stage at the accelerating beam of 80 kV. X-ray diffraction was performed with a Philips PW 1050/25 diffractometer equipped with a cobalt anticathode ($\lambda = 0.179$ nm).

Ultra-violet–visible (u.v.–vis.) absorption and fluorescence spectra were recorded on Unicam SP8-200 and Perkin–Elmer MPF44B instruments, respectively. Fluorescence spectra are uncorrected for photomultiplier (R928) response. Emission lifetimes were measured following excitation by single pulses (308 nm, 20 ns, 20–30 mJ) from a Lambda Physik EMG50 excimer laser using an R928 photomultiplier and recorded on a 125 MHz digital oscilloscope (Philips PM 3311C). Samples were contained in a 2 mm path-length quartz cell mounted at ~135° to the exciting beam and at ~135° to the emission beam.

Sample preparation

UO_2^{2+} or Eu^{3+} were incorporated into the membrane by soaking in stirred solutions containing appropriate concentrations of $UO_2(NO_3)_2 \cdot 6H_2O$ or $Eu(NO_3)_3 \cdot 6H_2O$. The amount of uranium absorbed by the membrane was calculated from the concentration of UO_2^{2+} in the solution before and after exchange by determination spectrophotometrically of its dibenzoylmethane complex[21]. Samples for spectroscopic studies were dehydrated by pumping under vacuum ($\sim 10^{-4}$ Torr) at temperatures in the range 290–420 K in a sealed 2 mm path-length quartz cell. The water content of the sample was estimated by weighing the sample after transfer in a glove bag filled with dry argon.

RESULTS

UO_2^{2+} was incorporated into Nafion by stirring samples of the H^+-form membrane in solutions of $UO_2(NO_3)_2$ (1–5 mM) at room temperature. It was observed that saturation occurred with a ratio of $U:SO_3^-$ of 0.5—as expected from the stoichiometry. Samples containing lower concentrations of uranium were prepared by stirring the membrane with stoichiometric amounts of UO_2^{2+}. Absorption occurs rapidly (within a few minutes), but samples were typically stirred for a period of 1 h so as to allow complete equilibration. UO_2^{2+} ions were incorporated into Flemion in a similar fashion but samples were stirred for a longer period (16 h) at a higher temperature (50°C) because of the known slower migration of metal ions into this perfluorocarboxylate membrane[5].

Electron microprobe analysis showed that for all samples the distribution of uranium was uniform across the membrane (on a micrometre scale), irrespective of the exchange ratio or type of membrane (see *Figure 1*). Two ultra-thin specimens of a fully exchanged Nafion sample ($U:SO_3^- = 0.5$) having thicknesses of respectively 900 and 400 Å were prepared and subjected to transmission electron microscopy (*Figures 2a* and *2b*). In both cases particles are observed that are not present in the H^+-form membrane. In the 900 Å sample the particles have an apparent average diameter of 40–50 Å, whereas in the 400 Å sample the observed diameter is 20–30 Å. This discrepancy is due to the overlapping of the particles through the thickness of the membrane, and the lower value should therefore be taken as the upper limit for the average diameter.

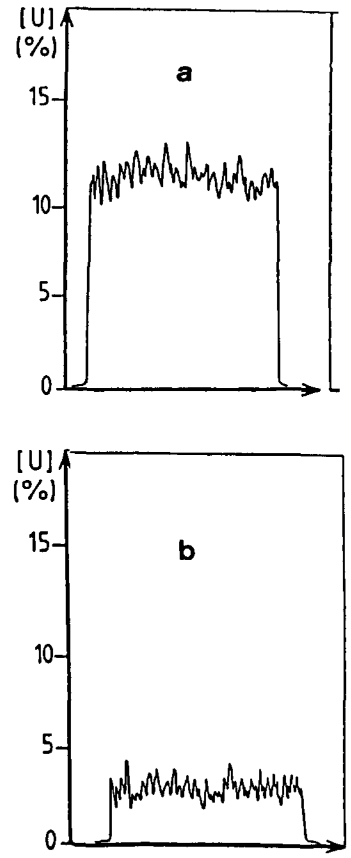

Figure 1 Electron microprobe analysis of the distribution of uranium in UO_2^{2+}-exchanged Nafion membranes: (a) $U:SO_3^- = 0.50$; (b) $U:SO_3^- = 0.20$

Spectroscopic and excited-state lifetime measurements

The absorption spectra of a Nafion membrane containing UO_2^{2+} ion ($U:SO_3^- = 0.20$) at various water contents are shown in *Figure 3*. It will be noted that the spectrum in the 27% hydrated membrane is closely similar to that of UO_2^{2+} in aqueous acidic solution (probably $UO_2(OH_2)_6^{2+}$). The shifting of the band maxima at lower water contents may be ascribed to coordination of the uranyl ion by a sulphonate group of the membrane material. Under extremely dry conditions the spectrum shows a considerable amount of fine structure. It has been reported that the principal factor controlling the structure of uranyl ion spectra is the symmetry imposed by the coordinated ligands[22]. The observed changes in spectra are therefore consistent with alterations in the molecular symmetry caused by the successive substitution of water molecules in the coordination sphere by sulphonate groups.

The emission spectra of the UO_2^{2+} in the 27% hydrated membrane consists of a series of bands (maxima at 472,

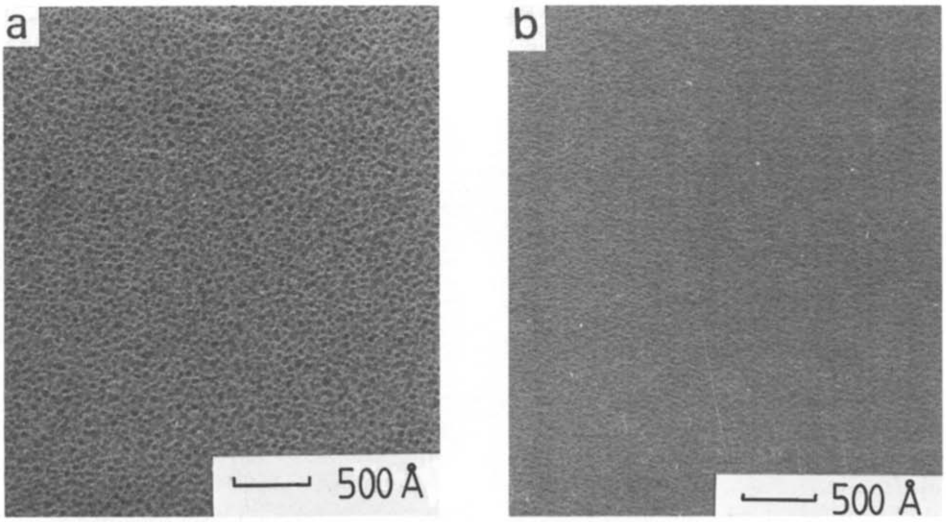

Figure 2 Transmission electron micrographs of a UO_2^{2+}-exchanged Nafion membrane ($U:SO_3^-$) = 0.50). Sample thickness: (a) 900 Å; (b) 400 Å

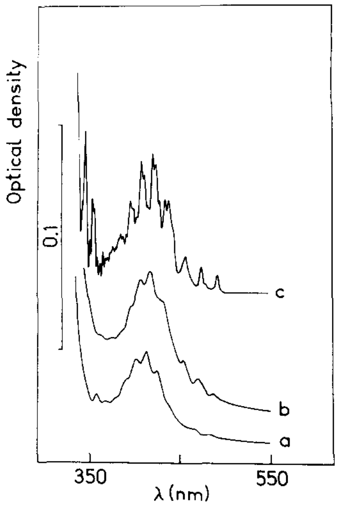

Figure 3 U.v.–vis. absorption spectra of UO_2^{2+}-exchanged Nafion membrane ($U:SO_3^- = 0.2$) with various water contents: (a) 27%; (b) 1.3%; (c) 0%. (For clarity, baseline has been displaced in each case)

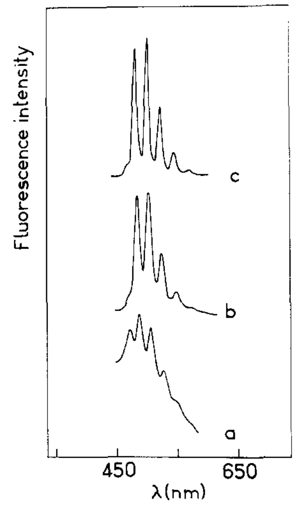

Figure 4 Luminescence spectra of UO_2^{2+}-exchanged Nafion membrane ($U:SO_3^- = 0.2$) with various water contents: (a) 27%; (b) 1.3%; (c) 0%. Emission intensity scales are different for each sample. (For clarity, baseline has been displaced in each case)

488, 511, 535 and 562 nm), consistent with that of aquated uranyl ion. On dehydration the band positions shift slightly (to 493, 516, 540, 568 and 600 nm), the resolution of the peaks becomes clearer, and the intensity is greatly enhanced (*Figure 4*). No splitting of these bands is noted in the completely dehydrated sample. For each sample the excitation spectrum closely resembles that of the absorption spectrum (for example, the same splitting is noted in the 0% water sample). It was also confirmed that the excitation and emission spectra of a more weakly exchanged sample ($U:SO_3^- = 0.02$) were similar to those of the 0.20 $U:SO_3^-$ sample, suggesting that interaction of the uranyl ions is not responsible for the observed band splitting in the dehydrated sample. The possibility that the band splitting was due to uranyl ion at different sites was studied by examining the emission spectrum following excitation at either of the peaks (e.g. at 420 and 424 nm). No difference in the emission spectrum was observed indicative of a single species being responsible for the observed absorption spectra.

The emission lifetime of the $U:SO_3^- = 0.20$ sample containing various amounts of water was recorded (*Table 1*). It may be noted that the lifetime varies by over two orders of magnitude. Good fits to a single-exponential decay were found over three half-lives, except at about 6% hydration. The increase in lifetime upon dehydration can be ascribed to the diminution of the concentration of water in the vicinity of the uranyl ion. (Similar behaviour was found for 0.02 M solutions of UO_2^{2+} in aqueous trifluoromethanesulphonic acid mixtures of varying composition.) That the excited-state decay can be fitted substantially by a single exponential may be taken as evidence for the equilibration of the various forms of the uranyl ion with the solvent within their lifetimes.

The absorption spectrum of UO_2^{2+} in Flemion, whether at ambient humidity or soaking in water, shows a broad band with maximum absorption at 419 nm, with shoulders at 410 and 426 nm, and two weak bands at 470 and 486 nm. Similar spectra were found for partially and totally exchanged samples. This spectrum, which is quite

Table 1 Effect of hydration on the fluorescence decay time of UO_2^{2+} in Nafion membrane ($U:SO_3^- = 0.20$). Excitation at 308 nm using XeCl laser

Hydration[a] (% H_2O)	Moles H_2O per mole sulphonate	τ (μs)
19	12	2.0
15	9.0	2.4
9.4	5.8	6.0
6.1	3.7	30
4.6	2.8	56
4.4	2.7	95
3.5	2.2	116
2.6	1.6	235
1.5	0.9	405
1.3	0.8	480
0.9	0.5	555
~0	0	640

[a] 100 × (wt of H_2O/wt of dry membrane)

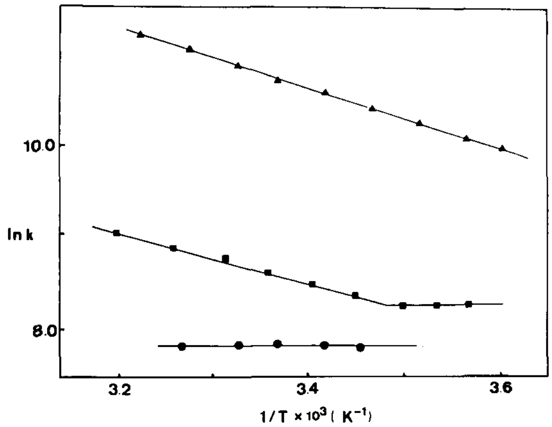

Figure 5 Arrhenius plots for the excited-state decay rate constant for UO_2^{2+} in Nafion membrane ($U:SO_3^- = 0.2$) with various water contents: (●) 1.5%; (■) 3.6%; (▲) 18%

different from that in aqueous solution or in Nafion, presumably indicates that the uranyl ion is bound to the membrane's carboxylate groups even when the membrane is water-saturated. This is in line with the behaviour found for other ions in Flemion[5]. The lifetime of emission in water-soaked Flemion membrane (12 μs) is also appreciably longer than that found for the ion in Nafion or aqueous solution. Removal of water by vacuum pumping of the membrane leads to non-exponential behaviour and an increase in the average lifetime.

It is known that the decay of the excited state of UO_2^{2+} in acidic aqueous solution is determined by a chemical deactivation process (probably involving reversible hydrogen abstraction) with an activation energy[8] of ~44 kJ mol^{-1}. *Figure 5* shows the Arrhenius plots for the excited-state decay for typical UO_2^{2+}-containing Nafion samples in the temperature range 275–325 K. For water content greater than 9%, an activation energy of 30 ± 2 kJ mol^{-1} is determined, whereas for the very dry membrane zero activation energy is found. For a sample containing 3.6% water the Arrhenius plot is biphasic, suggesting a changeover in the mechanism of deactivation. A membrane containing 12% water was studied down to 128 K. It was observed that for this sample the excited-state decay was markedly non-exponential in the temperature range 270–180 K, presumably indicating that equilibration of the sample is not complete within the lifetime of the excited state. At temperatures below 180 K the kinetics again became predominantly single-exponential. Lifetimes recorded were 255 μs (169 K), 290 μs (157 K), 293 μs (145 K), 300 μs (133 K) and 308 μs (128 K).

The transfer of electronic energy between UO_2^{2+} and Eu^{3+} has been suggested as a means of studying the morphology of membranes[23] by analogy with methods used for the study of micelles[24]. We therefore considered it of interest to study briefly how energy transfer would depend on membrane hydration and on changing from perfluorosulphonate membranes to perfluorocarboxylate materials. Energy transfer was evidenced by both excitation and emission spectra and by time-resolved emission measurements. The emission of Eu^{3+} is characterized by a series of lines, corresponding to $^5D_0$–^7F_n transitions, and it is well known that the europium ion lifetime and spectra are sensitive to the presence of water in its coordination shell (and thus to water in the surrounding medium). Drying out Nafion membranes results in both an increase in lifetime and a change in the relative intensities of the $^5D_0$–$^7F_1$ and $^5D_0$–$^7F_2$ transitions[25,26]. In the present study energy transfer between UO_2^{2+} and Eu^{3+} has been compared in Nafion ($U:Eu:SO_3^- = 0.15:0.18:1.0$) and Flemion ($U:Eu:CO_2^- = 0.10:0.10:1.0$) samples). In the Nafion sample both the emission spectra (excited at a wavelength where Eu^{3+} does not absorb) and the excitation spectra for the Eu^{3+} emission reveal energy transfer in samples at ambient hydration (~8%) or when the membrane is further dried (*Figures 6a* and *6b*). The extent of energy transfer, as judged by the excitation spectrum, does not appear to vary much with hydration below 8%. When the sample is fully hydrated (by soaking in water) no evidence for energy transfer was found. This may be attributed to the short lifetime of UO_2^{2+*} under these conditions, the lower quantum yield of emission of the Eu^{3+} in the hydrated membrane and probably to a reduced rate of energy transfer under these conditions. By contrast, in the Flemion membrane energy transfer is much more complete (*Figures 6c* and *6d*) and is observed also in fully hydrated samples. After excitation of the UO_2^{2+} with a 308 nm laser pulse both the decay of the UO_2^{2+} emission and the concurrent grow-in of that of Eu^{3+} have been monitored.

Treatment of UO_2^{2+}-containing Nafion membranes with KOH

Samples of UO_2^{2+}-containing Nafion membranes, either completely ($U:SO_3^- = 0.50$) or partially exchanged ($U:SO_3^- = 0.20$), were treated by immersion in KOH solutions having concentrations ranging from 0.02 to 5 M. The distribution of uranium across the membrane was examined by electron microprobe analysis. Some typical results are shown in *Figure 7*. It will be observed that treatment with KOH causes concentration of the uranium near the edges of the membrane. This concentration effect increases with time of soaking (*Figure 7A*) and is more pronounced for lower concentrations of KOH (compare *Figure 7B* (a) and (b)) and for partially exchanged membranes (see *Figure 7C*). This behaviour is similar to that observed for Fe(III)- and Ru(III/IV)-containing membranes[14,17], where treatment with KOH produces hydrated metal oxides. Transmission electron microscopy of a sample close to the surface appears to show (*Figure 8*) that the uranium is in the form of particles of diameter between 50 and 600 Å, although closer

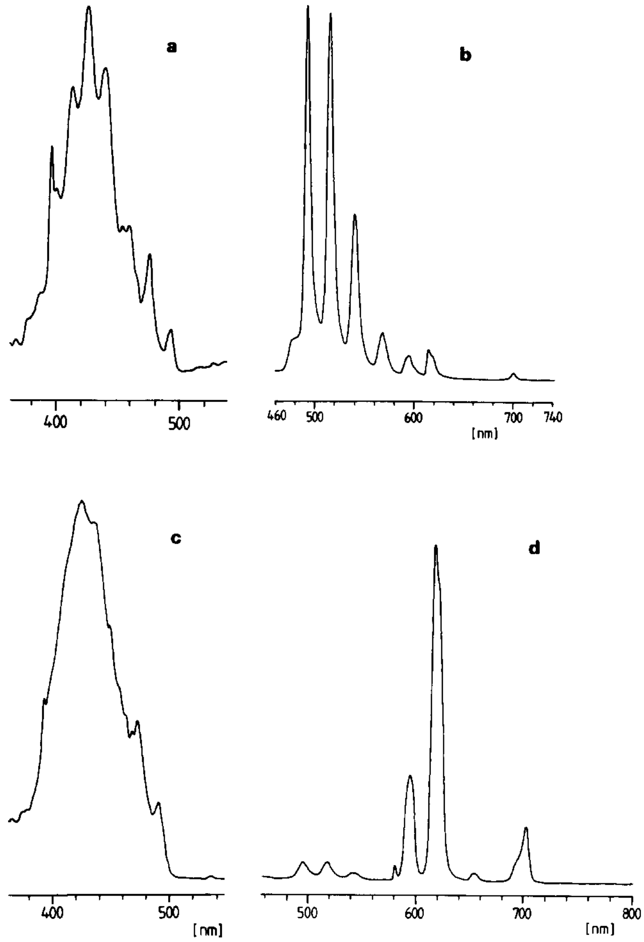

Figure 6 Emission and excitation spectra for Nafion and Flemion membranes containing both UO_2^{2+} and Eu^{3+}. Samples are dehydrated by vacuum pumping at 100°C for 2 h. (a) and (b) Nafion ($U:Eu:SO_3^- =$ 0.15:0.18:1.0): (a) excitation spectrum with λ(emission at 615 nm; (b) emission spectrum with λ(excitation) at 420 nm. (c) and (d) Flemion ($U:Eu:CO_2^- = 0.10:0.10:1.0$): (c) excitation spectrum with λ(emission) at 615 nm; (d) emission spectrum with λ(excitation) at 424 nm

examination reveals that the larger agglomerates consist of particles of 50–100 Å.

It is known that, depending on concentration and pH, uranyl ion in solution may form a number of species, some of which can be distinguished by their spectroscopic[7] and X-ray powder diffraction properties[20], and we have carried out such measurements in the hope of identifying the species present in the membrane. *Figure 9* shows the absorption and luminescence spectra of samples treated with 0.2, 1 and 5 M KOH. It may be observed that the spectra are strikingly different from those found for untreated UO_2^{2+}-containing membranes (*Figures 3* and *4*). However, they have similar features to samples of UO_2^{2+} ion in solutions of pH 5–7, prepared by treating UO_2^{2+} (1×10^{-2} M) with KOH in the stoichiometric range $U:OH^- = 1:2.5$–$1:3$. The two side-bands observed in the absorption spectrum of the sample of the 0.2 M KOH-treated Nafion sample are also characteristic of a sample prepared by reaction in solution of UO_2^{2+} and KOH ($U:OH^- = 1:2.5$; resultant pH = 5.6), whereas the spectra of membranes treated with 1 M or 5 M KOH more closely resemble the spectra of solution species formed by reaction in solution of UO_2^{2+} and KOH ($U:OH^- = 1:2.5$–$1:3$; resultant pH = 6–7). The fluorescence spectra in the solution and membranes are also similar, although in some cases the bands are blue-shifted in the membrane, possibly a result of partial dehydration or due to the membrane matrix.

X-ray diffraction and electron microdiffraction measurements have been carried out in order to determine whether the particles produced are crystalline and to aid in the identification of these compounds by comparison with literature values for various oxides, hydroxides and uranate species[27,28]. A typical X-ray diffraction pattern (of a sample prepared by treatment with 0.2 M KOH) and a microdiffraction photograph of the same sample are shown in *Figure 10*. The broad peaks (at $2\theta = 14.5$, 31.0, 34.9, 47.0, 53.5 and 63.0 deg, i.e. $d_\beta = 6.7$, 3.2, 2.9, 2.15, 1.9 and 1.64 Å) and the microdiffraction data ($d_\beta = 1.66$ and 0.90 Å) are consistent with a mixture of different-sized crystallites which may correspond to slightly different structures. As the principal features of the pattern for '$UO_3 \cdot 2H_2O$' can be found in this pattern, it is probable that this species is the dominant component,

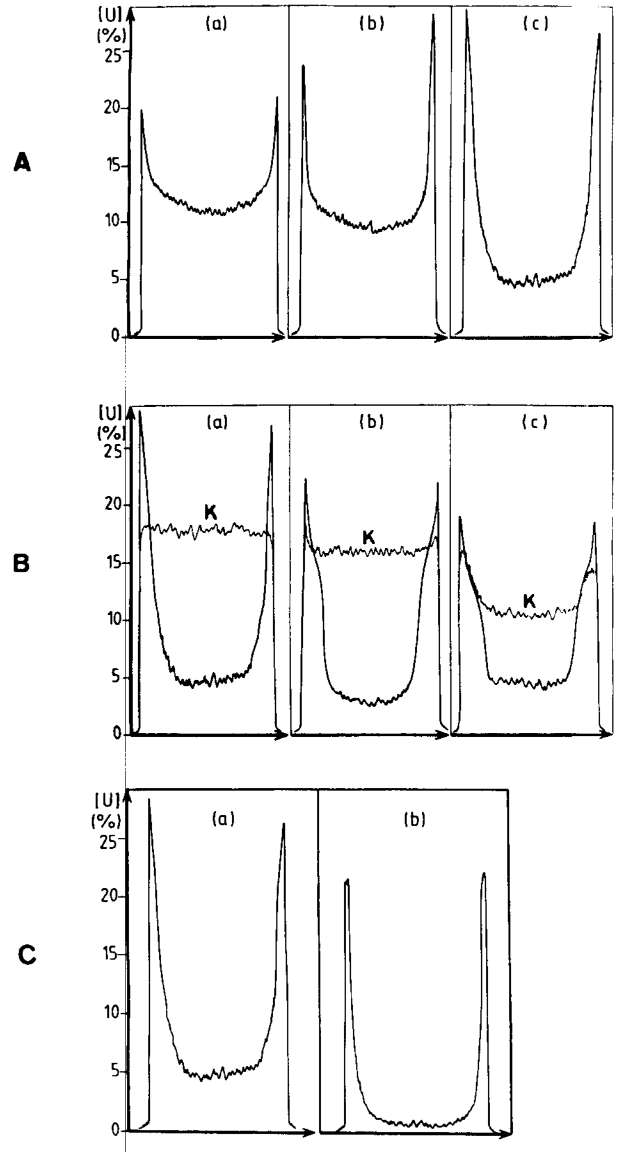

Figure 7 Electron microprobe analysis of the distribution of uranium in UO_2^{2+}-exchanged Nafion membranes treated with KOH solutions. (A) $U:SO_3^- = 0.50$ treated with 0.2 M KOH for (a) 15 min, (b) 45 min and (c) 180 min. (B) $U:SO_3^- = 0.50$ treated for 180 min with (a) 0.2 M, (b) 1.0 M and (c) 5.0 M KOH. Also shown, on an arbitrary scale, are K^+ distributions. (C) UO_2^{2+}-exchanged Nafion membranes treated with 0.2 M KOH solutions for 120 min: (a) $U:SO_3^- = 0.50$; (b) $U:SO_3^- = 0.20$

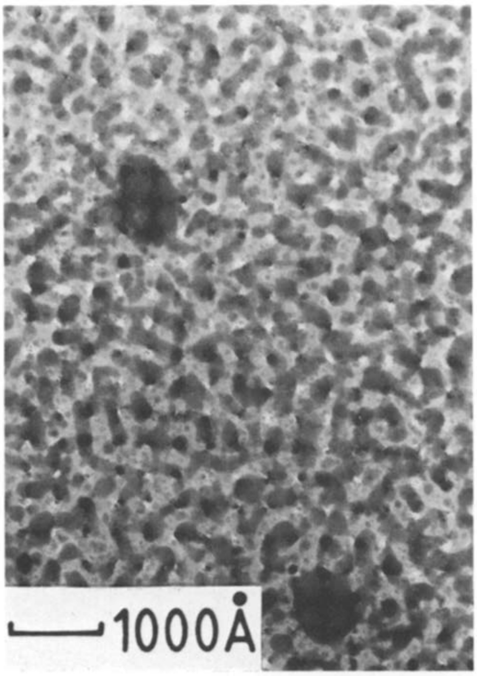

Figure 8 Transmission electron micrograph of a partially UO_2^{2+}-exchanged Nafion ($U:SO_3^- = 0.20$) membrane treated with 0.2 M KOH for 3 h

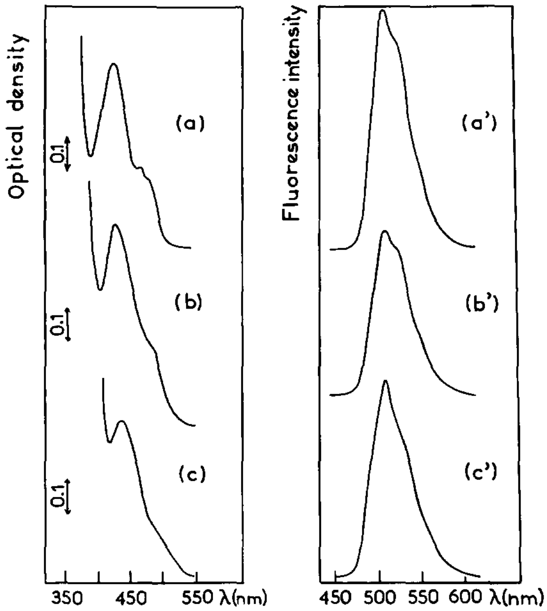

Figure 9 Absorption (a)–(c) and luminescence (a')–(c') spectra of partially UO_2^{2+}-exchanged Nafion ($U:SO_3^- = 0.20$) membranes after treatment for 3 h with KOH of differing concentration: (a) 0.2 M; (b) 1.0 M; (c) 5.0 M

although the variability in the diffraction patterns obtained from samples prepared by identical procedures indicates that the proportion of this species present in the membrane also varies. Samples prepared by treatment with stronger KOH solutions showed features consistent with the presence of some uranates in the membranes and this is consistent with the potassium profiles observed with these samples (*Figure 7B*).

CONCLUSIONS

The above results show that UO_2^{2+} is a very sensitive probe for the hydration of perfluorinated membranes such as Nafion and Flemion. The very marked variations in the absorption spectra and especially in the excited-state lifetime of UO_2^{2+} upon dehydration of Nafion membranes are consistent with the displacement of coordinated water by SO_3^- groups of the membrane. The fact that at room temperature the decay is single-exponential for most extents of hydration indicates that under these conditions there is rapid exchange of the coordinated water and a consequent equilibration of the species. The role of water in determining the decay lifetime is also demonstrated by the Arrhenius behaviour of samples of differing hydration. The activation energy observed for the strongly hydrated sample ($30 \pm 2\,kJ\,mol^{-1}$) is similar to that observed in other hydrated media[8], and has been ascribed to a chemical deactivation process probably involving reversible hydrogen abstraction. The essentially temperature-independent decay observed for the very dry samples is consistent with a physical mechanism for the decay or possibly with proton tunnelling[9]. For the 12% sample, which was studied to low temperature, it was found that the rate constant levelled off at a lifetime of $\sim 300\,\mu s$ at temperatures below 150 K. As a study of nuclear magnetic resonance (n.m.r.) relaxation data[29] has indicated that hydrated H^+-form Nafion shows a glass transition temperature of the water phase near 170 K, it is possible that restricted motion in the water could be responsible for the levelling off of the rate of decay of the excited state in this temperature range. The observation that below 270 K the 12% hydrated Nafion sample displayed non-exponential behaviour either indicates that the

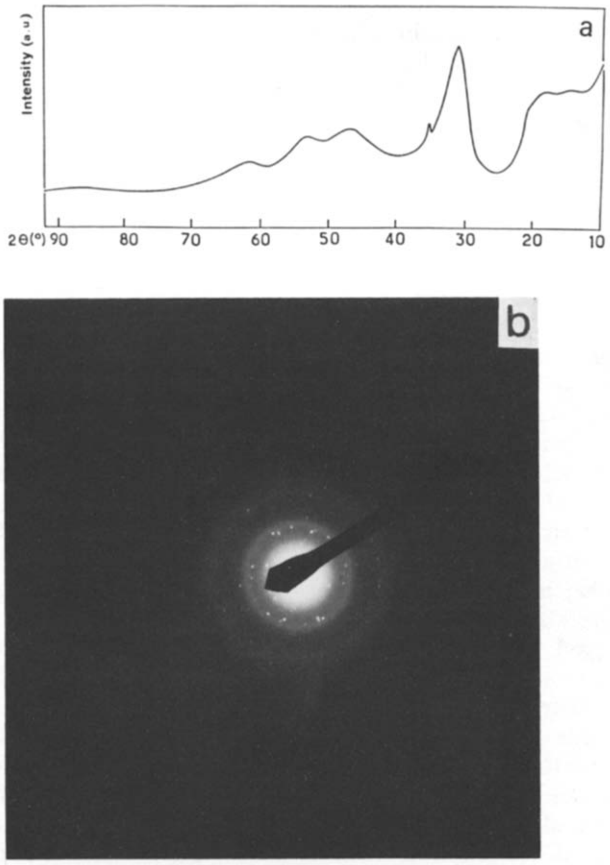

Figure 10 (a) X-ray diffraction and (b) electron microdiffraction for a completely UO_2^{2+}-exchanged Nafion ($U:SO_3^- = 0.50$) membrane treated with 0.2 M KOH for 3 h

exchange of water from the sample excited state is strongly reduced or it may be due to the marked reduction in the mobility of water below the freezing point of water previously monitored by n.m.r.[30].

Marked differences have been found between the behaviour of UO_2^{2+} in Flemion and Nafion. This is most readily seen from the absorption spectra and excited-state lifetimes in water-soaked membranes, both of which indicate that the uranyl ion is coordinated to the carboxylate groups of the Flemion membrane under these conditions. Although Flemion is known to take up less water than Nafion[5], this is insufficient to account for the observation, and the difference of behaviour in Flemion and Nafion membranes should be ascribed to the greater stability of uranyl carboxylates compared to uranyl sulphonates. The non-exponential excited-state lifetime observed for the ion in dried membrane at room temperature may be attributed to slow equilibration between the various carboxylate complexes present in the membrane under these conditions. The strong binding of other metal ions to the carboxylate group in such membranes has already been noted[5], and this no doubt influences the ability of metal ions to quench the excited states of organic molecules in Flemion[31].

Particularly different behaviour of Flemion and Nafion is found for membranes containing both UO_2^{2+} and Eu^{3+}, where the efficiency of energy transfer is far greater for the perfluorocarboxylate material. This greater efficiency of energy transfer is most probably a consequence of the formation of carboxylate complexes containing both UO_2^{2+} and Eu^{3+}, in which energy transfer is efficient[32], rather than to a feature of ion clustering in the membranes.

The observed precipitation of uranyl ions within the Nafion membrane by soaking in KOH solution is similar phenomenologically to the behaviour found with Fe(III) and Ru(III/VI)[14,17]. As in those cases, it is found here that the precipitates are not dispersed uniformly across the membrane but rather are concentrated near the membrane surface, with the precise profile depending on the conditions used. This feature can be explained by a simple model, which was first put forward to explain the behaviour of iron oxides[33]. When the UO_2^{2+}-exchanged Nafion is soaked in KOH solution, K^+ ions diffuse from the solution into the membrane and displace the UO_2^{2+}. These latter migrate through the membrane until they meet a sufficient concentration of OH^- to precipitate them as the hydrous oxide or uranate. The driving force for migration is the concentration gradient of the species. This simple model therefore predicts that precipitation will initially occur close to the surface and that a relatively sharp profile will form if, as expected, the K^+ ion diffuses much more rapidly than the OH^- and the exchange between UO_2^{2+} and K^+ is rapid. This is indeed what is found (*Figure 7*). Clearly precise modelling would require a knowledge of the diffusion coefficients in Nafion of the various species involved (K^+, OH^- and UO_2^{2+}). It is interesting that the spectroscopic studies show that the species produced in the membrane are similar to those present in solutions of pH 5–7, even though the pH outside the membrane is 13 or greater. This may be attributed in part to the exclusion of OH^- from the anionic membrane. It is also to be noted, however, that the reaction gives rise to a mixture of compounds—that is, that the membrane does not force the exclusive formation of a single species.

The present studies point to the concentration profile being a general phenomenon for the *in situ* precipitation of hydroxides/oxides of a wide range of metals. Other experiments have shown related phenomena for the reduction of metal ions by borohydride ion. Such procedures have been successfully used for the preparation of extra-fine platinum particles dispersed in Nafion and used in solid polymer electrolytes for water electrolysis[16].

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